Accurate adiabatic potential energy surface for $1^2A'$ state of FH$_2$ based on ab initio data extrapolated to the complete basis set limit

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Abstract. An accurate single-sheeted double many-body expansion potential energy surface is reported for the title system. It is obtained by using the aug-cc-pVTZ and aug-cc-pVQZ basis sets with extrapolation of the electron correlation energy to the complete basis set limit, plus extrapolation to the complete basis set limit of the complete-active-space self-consistent field energy. The collinear and bending barrier heights of the new global potential energy surface is 2.301 and 1.708 kcal mol$^{-1}$, in very good agreement with the values of 2.222 and 1.770 kcal mol$^{-1}$ from the current best potential energy surface. In particular, the new potential energy surface describes well the important van der Waals interactions which is very useful for investigating the dynamics of the title system. Thus, the new potential energy surface can both be recommended for dynamics studies of the F + H$_2$ reaction and as building block for constructing the potential energy surfaces of larger fluorine/hydrogen containing systems. Based on the new potential energy surface, a preliminary theoretical study of the reaction F($^2P$) + H$_2$(X$^1\Sigma^+$) \rightarrow FH(X$^1\Sigma^+$) + H($^3S$) has been carried out with the methods of quasi-classical trajectory and quantum mechanical. The results have shown that the new PES is suitable for any kind of dynamics studies.

1 Introduction

The F + H$_2$ reaction is one of the most extensively studied elementary chemical reactive processes, both experimentally and theoretically. Total and angular cross sections, rate constants, and product vibrational-rotational state populations are the primary quantities that have been probed for this reaction [1]. For many years, theorists have had serious difficulty in reproducing a qualitatively correct picture of the experimental results [2–6] for such a reaction. This has been due both to the lack of sufficient computer power to perform very accurate quantum scattering calculations, and of a sufficiently high quality potential energy surface (PES). Recent advances in techniques for the treatment of reaction dynamics [7–13] have meant that accurate reaction cross sections can now be obtained for triatomic systems using essentially exact quantum mechanical (QM) methods, provided that an accurate PES is available. Recently, a series of experiments, using high the resolution and highly sensitive H-atom Rydberg tagging method were reported by Yang and co-workers [14–17], who studied the title reaction in great detail [17].

The first ab initio PES was calculated by Bender et al. [18] using the configuration interaction method at single reference level. This predicted a collinear transition state for the title reaction with a barrier height of 1.66 kcal mol$^{-1}$. Subsequent attempts to refine the transition state by employing increasingly larger basis sets and using the multireference configuration interaction (MRCI) method as well as fourth-order perturbation theory (MP4) led to barriers higher than 3.2 kcal mol$^{-1}$, at variance with the experimental data. In 1985, Schaefer [19] estimated the lowest possible limit to the barrier height from ab initio calculations to be 2.35 kcal mol$^{-1}$. Truhlar and co-workers [20–25] then made a significant advance by finding and characterizing the bent transition state using a scaled electron correlation approach. These PESs have been denoted T5 [20], T5A [21], 5SEC [24] and 6SEC [25], respectively, with 5SEC employing an early version of double many-body expansion (DMBE [26–29]) theory to be examined below in further detail. Bauschlicher et al. [30] improved matters further by using a large enough orbital basis and including the effect of higher than double excitations on the correlation energy. In 1996, Stark and Werner [31] calculated a new and more accurate ab initio
PES (here denoted SW), using the internally contracted MRCI method with complete active space self-consistent reference function. In the past few years, a number of new PESs have been constructed in order to interpret the corresponding experiments. Specifically, Xu et al. [32] constructed a MRCI + Q level using the aug-cc-pV5Z basis set (such basis are generally denoted as AVXZ, with X being usually referred to as the basis-set cardinal number) of PES, which was found to be able to accurately predict the resonance states in the F + H2 reaction [14,17]. Meanwhile, Li et al. [33] carried out MRCI + Q/AV5Z calculations and fitted two PESs for the FH2 system (denoted LWA-5 and LWA-78, according to the value of empirical factor utilized to scale the correlation energy, respectively 1.05 and 1.078). More recently, Fu et al. [17] applied a new scheme to construct an accurate ground state PES (denoted FXZ) for the title system using the coupled-cluster method and a large basis set. It should be noted that based on different PESs, large variations are seen for energy barriers of the collinear and bent transition states of the F + H2 reaction, since the barrier height is quite sensitive to wave function, basis set, and electron correlation effects. Indeed, the results for it range from around 1.5 kcal mol$^{-1}$ [18,22,30,34–37] to more than 3.0 kcal mol$^{-1}$ [38–40].

The major goal of the present work is to report an accurate ab initio global adiabatic PES for the ground state of FH2 based on DMBE theory [26–29]. This approach has been successfully applied to a wealth of triatomic systems (such as recently DMBE PESs for ground state [41,42] and excited-states [43–45] of NH3) as well as tetraatomic (O4 [46], HO3 [47], HSO2 [48], NH3 [49,50] and N2H2 [51]), and even larger polyatomic (HO4 [52] and HO5 [53]) systems. Being a fragment of larger F$\cdot$H$\cdot$ species like those of relevance in studying the synthesis of FH2, such a PES may then be of use in constructing DMBE forms for those larger systems. Indeed, this may be yet another motivation for modeling an accurate single-sheeted DMBE PES for the title system. To calibrate such a DMBE form, 1875 ab initio points have been calculated in the present work at the MRCI level based on the full-valence-complete-active-space (FVCAS, later denoted simply as CAS) reference wave function. The popular Davidson correction has also been employed to account for quadruple excitations, MRCI + Q. Both AVTZ and AVQZ atomic basis sets of Dunning [54] have been employed. As it is well known, to obtain a chemically accurate PES, large basis sets are usually required. Rather than utilizing such basis sets, we extrapolate the total energy to the complete basis-set (CBS) limit by employing the uniform singlet-pair and triplet-pair (USTE [55,56]) scheme. Indeed, an asset of USTE is to allow accurate CBS extrapolations even when utilizing reasonably modest basis sets such as those here employed. As a result, significant savings of computer time are obtained. As usual in DMBE theory [26–29], the PES shows the correct long-range behavior at all dissociation limits.

The paper is organized as follows. Section 2 describes the ab initio calculations, while the analytical representation of the PES is reported in Section 3: of the two-body energy terms in Section 3.1, and three-body ones in Section 3.2. The main topographical features of the FH2 (1$^2\Lambda'$) adiabatic PES will be examined in Section 4, and some conclusions gathered in Section 5.

2 Computational details

2.1 Ab initio calculations

To map the PES, a total of 1875 points have been calculated for F − H2 regions defined by 1.2 ≤ RH0/\(a_0\) ≤ 3.6, 1.4 ≤ rFH−H2/\(a_0\) ≤ 10, and 0 ≤ \(\gamma/\text{deg}\) ≤ 90 while, for H − FH, they cover geometries defined by 1.6 ≤ RHFH/\(a_0\) ≤ 3.6, 1.4 ≤ rFH−FH/\(a_0\) ≤ 10, and 0 ≤ \(\gamma/\text{deg}\) ≤ 180; \(R, r,\) and \(\gamma\) are atom-diabit Jacobi coordinates. All ab initio calculations have been carried out at the MRCI + Q [57,58] level of theory with the MOLPRO [59] package, using the FVCAS [57] wave function as reference. The AVTZ and AVQZ atomic basis sets of Dunning [54] have been employed. This involves 7 correlated electrons in 6 active orbitals (5a$^+$ + 1a$^-$), amounting to a total of 92 and 172 configuration state functions with AVTZ and AVQZ atomic basis sets, respectively. To accelerate convergence of the correlation energy to the one electron complete basis set (CBS) limit, the USTE scheme is employed. In all calculations, the core is kept frozen and relativistic effects ignored. Despite being a seemingly unacceptable simplification when aiming at high-accuracy requirements, its impact will be clarified along the paper. Of course, such improved calculations should, for consistency, not be done with the standard basis sets described above but with correlation consistent core-valence ones. Along this line of reasoning, one should further recall that other effects, often of competitive magnitude, are altogether also neglected, namely, relativistic and nonadiabatic ones. A final pragmatic reason for improving cost-effectiveness of the calculations stems from the observation that the data are going to be modeled with an accuracy that probably falls close to or even exceeds the error that can be attributed to the neglect of such core correlation effects [43].

2.2 Extrapolation scheme

Built in a systematic manner that is intended to relate the correlation energy to the cardinal number \(X\), Dunning’s correlation consistent basis sets allow the extrapolation of the raw energies to the one-electron CBS limit. To perform the extrapolation, the MRCI + Q energy is treated as usual in split form by writing [55]

\[
E_X(R) = E_X^{\text{CAS}}(R) + E_X^{\text{dc}}(R)
\]  

where the subscript \(X\) indicates that the energy has been calculated in the AVXZ basis, and the superscript dc stands for the dynamical correlation energy. Note that all extrapolations are carried pointwise, and hence the vector \(R\) of the nuclear geometrical coordinates will be omitted for simplicity.
To extrapolate the CAS energy (uncorrelated in the sense of lacking dynamical correlation), a proposed \cite{ref55} generalization of the protocol adopted by Karton and Martin \cite{ref60} (KM) to extrapolate single-reference self-consistent-field energies is utilized,
\[ E_X^{\text{CAS}} = E^{\text{CAS}}_{\infty} + B/X^\alpha \]  \hspace{1cm} (2)
where $\alpha$ is a predefined constant. Being a two-parameter protocol ($E^{\text{CAS}}_{\infty}, B$), a minimum of two raw energies will be required for the extrapolation. Specifically, equation (2) will be calibrated from the CAS/AV($T, Q$) $E$ energy pairs, using a value of $\alpha = 5.34$ which has been found optimal when extrapolating HF energies to the CBS limit.

For the dynamical correlation, a popular two-parameter CBS protocol is \cite{ref61}
\[ E^{\text{dc}}_X = E^{\text{dc}}_{\infty} + \frac{A_3}{(X + \alpha)^3} + \frac{A_5}{(X + \alpha)^5} \]  \hspace{1cm} (3)
where $E^{\text{dc}}_X$ is the dynamical correlation energy obtained with the $X$-tuple basis set. Although equation (3) is known to perform accurately when extrapolating from energies based on large cardinal number pairs, its performance is significantly less satisfactory when using ($T, Q$) pair. A more reliable scheme is the recently suggested USTE \cite{ref55} scheme (see also Ref. \cite{ref62}). This has its basis on the three-parameter protocol
\[ E^{\text{dc}}_X = E^{\text{dc}}_{\infty} + \frac{A_3}{(X + \alpha)^3} + \frac{A_5}{(X + \alpha)^5} \]  \hspace{1cm} (4)
with the auxiliary relation
\[ A_5 = A_5(0) + cA^m_3 \]  \hspace{1cm} (5)
where $E^{\text{dc}}_{\infty}$, $A_3(0)$, $A_3$, $c$, $m$, and $\alpha$ are parameters. By fixing $\alpha$, $A_3(0)$, $c$ and $m$ from other criteria (utilizing ab initio data), equation (4) can then be transformed into a ($E^{\text{dc}}_{\infty}$, $A_3$) two-parameter rule \cite{ref55}. Using USTE, it has been shown in reference \cite{ref55} that both the full correlation in systems studied by the popular single-reference Møller-Plesset (MP2) and coupled cluster [CCSD and CCSD(T)] methods as well as its dynamical part in MRCI + Q calculations can be accurately extrapolated to the CBS limit. In particular, for the dynamical correlation of 24 systems studied \cite{ref55} using the MRCI + Q method, the optimum values of the "universal-like" parameters were found to be $A_3(0) = 0.0037685459$, $c = -1.17847713E^{n−1/4}_n$ and $m = 5/4$, with $\alpha = -3/8$. In the present work, we will then utilize the USTE/($T, Q$) scheme to extrapolate the dynamical correlation energy of FH$_2$. As noted elsewhere \cite{ref43} for NH$_2$(1$^2\text{A}'$), since electronic degeneracies are often present in global PESs, including the present one, this may pose a subtle issue to extrapolation. In fact, not only the location of the CI may differ in the two chosen bases but also a given basis set may prove to have somewhat different qualities when utilized for different electronic states \cite{ref63}. Since this may cause small distortions on the data to be fitted, we advocate to place the raw ab initio points slightly away from such topological features and interpolate the CBS extrapolated data subsequently using the chosen functional form, here DMBE.

### 3 Single-sheeted DMBE potential energy surface

For the title system, the spin-spatial Wigner-Witmer rules predict the following dissociation scheme
\[ \text{FH}_2 (1^2\text{A}') \rightarrow F(2\text{P}) + H_2(X^1\Sigma^+ \gamma_9) \]  \hspace{1cm} (6)
\[ \rightarrow \text{FH}(X^1\Sigma^+) + \text{H}(^2\text{S}) \]  \hspace{1cm} (7)
\[ \rightarrow F(2\text{P}) + \text{H}(^2\text{S}) + \text{H}(^2\text{S}). \]  \hspace{1cm} (8)
Within the framework of DMBE theory \cite{ref64,ref65}, the single-sheeted PES is written as:
\[ V(R) = \sum_{x=EHF,dc} \left[ \sum_{i=1}^{3} V_x^{(2)}(R_i) + V_x^{(3)}(R) \right] \]  \hspace{1cm} (9)
where $R$ is the vector of the three intermolecular coordinates $R_j$ ($j = 1, \ldots, 3$), and $V_x^{(2)}$ and $V_x^{(3)}$ the two- and three-body terms in the cluster expansion of the CAS (this will be denoted as extended-hartree-Fock, EHF) and dynamical correlation energies.

As usual in the DMBE formalism, the EHF contributions are calibrated by fitting ab initio data to a suitable, physically motivated, functional form. In turn, the dc energies are modeled to a function that uses ab initio long-range dispersion energy (as well as electrostatic and induction when judged relevant) coefficients, eventually estimated at the same level of ab initio theory. Thus, no empirical information is required for the construction of the final PES using DMBE theory. The following sections give the details of the specific forms that are employed in equation (9).

#### 3.1 Two-body energy terms

The potential curves for the two-body fragments are based on the extended Hartree-Fock approximate correlation energy method for diatomic molecules including the united atom limit \cite{ref66} (EHFACE2U), and hence show the correct behavior at the asymptotic limits when $R \rightarrow 0$ or $R \rightarrow \infty$. They are given by the sum of $V_{\text{EHF}}^{(2)}$ and $V_{\text{dc}}^{(2)}$ contributions for each pair. Specifically, the two-body EHF term is written as:
\[ V_{\text{EHF}}^{(2)}(R) = -\frac{D}{R} \left( 1 + \sum_{i=1}^{n} a_i r_i \right) \exp(-\gamma r) \]  \hspace{1cm} (10)
\[ + \chi_{\text{exc}}(R) V_{\text{asy}}^{\text{exc}}(R) \]
where
\[ \gamma = \gamma_0[1 + \gamma_1 \tanh(\gamma_2 r)], \]  \hspace{1cm} (11)
and
\[ V_{\text{asy}}^{\text{exc}}(R) = -\tilde{A} R^5 \left( 1 + \tilde{a}_1 R + \tilde{a}_2 R^2 \right) \exp(-\tilde{\gamma} R) \]  \hspace{1cm} (12)
is the asymptotic exchange energy, $\chi_{\text{exc}}(R)$ a convenient damping function that accounts for charge overlap effects,
and \( r = R - R_e \) the displacement coordinate relative to equilibrium. In turn, the two-body dynamical correlation assumes the form
\[
V^{(2)}_{dc}(R) = - \sum_{i=0,8,10} C_n \chi_n(R) R^{-n}
\]
where
\[
\chi_n(R) = \left[ 1 - \exp \left( -A_n \frac{R}{\rho} - B_n \frac{R^2}{\rho^2} \right) \right]^n
\]
is a dispersion damping function, and \( A_n = \omega_0 n^{-\omega_1} \) and \( B_n = \beta_0 \exp(-\beta_1 n) \) are auxiliary functions [26,67]; \( \omega_0 = 16.36606 \), \( \omega_1 = 0.70172 \), \( \beta_0 = 17.19338 \), and \( \beta_1 = 0.09574 \). In turn, for the atom-pair XY, the scaling parameter is defined by \( \rho/a_0 = 5.5 + 1.25 (r_{XY}^{1/2} + r_{XY}^{1/2}) \). Finally, the coefficients in equations (10)–(14) are chosen to reproduce available theoretical data for the diatomic as described elsewhere [26,66]. For a slightly improved accuracy, the EHFACE2U potential energy curve for the ground state \( \text{H}_2(X^1\Sigma^+_g) \) reported in reference [68] has been adopted in the present work.

For hydrogen fluoride, \( \text{FH}(X^1\Sigma^+) \), the potential curve has been chosen to mimic the CBS/MRCl + Q ab initio energies here reported. All parameters are gathered in Table S1 of the Supplementary Information* (SI). Based on the fitted diatomic potentials of \( \text{FH}(X^1\Sigma^+) \), we calculated some spectroscopic constants which are listed in Table 1. The agreement with the experimental data is excellent and also with other accurate theoretical work.

### 3.2 Three-body energy terms

The three-body dynamical correlation is written as [68]
\[
V^{(3)}_{dc} = - \sum_i \sum_n f_i(R) C^{(i)}_n (R_i, \theta_i) \chi_n(r_i) r_i^{-n}
\]
where \( r_i, \theta_i \) and \( R_i \) are the Jacobi coordinates corresponding to a specific atom-diatom arrangement of the triatomic and \( f_i = \frac{1}{2} \{ 1 - \tanh[\xi (n R_i - R_j - R_k) / 2] \} \) is a switching function. Following recent work on \( \text{NH}_2(1^2A') \) [64] and \( \text{NH}_2(1^2A') \) [43], the parameters have been fixed at \( \eta = 6 \), \( \xi = 1.0 a_0^{-1} \) and \( \rho = 16.125 a_0 \). Regarding \( \chi_n(r_i) \), equation (14) is still adopted but \( R \) is replaced as usual by the center-of-mass separation for the relevant atom-diatom channel. In turn, the atom-diatom dispersion coefficients in equation (15) assume their typical form
\[
C_n^{(i)}(R_i) = \sum_L C^L_n(R_i) P_L(\cos \theta_i)
\]
where \( P_L(\cos \theta_i) \) denotes the \( L \)th Legendre polynomial. The expansion in equation (16) has been truncated by considering only the coefficients \( C^0_n, C^2_n, C^4_n, C^6_n \) and \( C^8_n \); all other coefficients are assumed to make a negligible contribution, and hence neglected. As usual, the atom-diatom dispersion coefficients assume the form
\[
C_n^{L,AB} = C_n^{L,AB} + C_n^{L,AC} + D_M \left( 1 + \sum_{l=1}^{3} a_l r^l \right)
\]

Since equation (16) is known to cause an overestimation of the dynamical correlation energy at the atom-diatom dissociation channels [68]. Thence, the two-body dynamical correlation energy for the \( ij \) pair has been multiplied by \( \Pi_{j<k}(1 - f_j) \). This ensures [68,69] that the only two-body contribution at the \( ij \) channel will be by the \( jk \) one. In turn, \( C_n^{L,AB} \) in equation (16), for \( L = 0 \), are the corresponding atom-atom dispersion coefficients which are given in Table S1 of the SI; for \( L \neq 0 \), \( C_n^{L,AB} = 0 \). Similarly, the least-squares parameters \( D_M, a_l, a_0, b_l, b_0 \) in equations (15)–(17) are collected in Table S2 of the SI. In turn, the internuclear dependences of \( C_n^{L,AB} \) are displayed in Figure S1 of the SI. Note that, for \( R = 0 \), the isotropic component of the dispersion coefficient is fixed at the corresponding value in the \( A-X \) pair, where \( X \) represents the united atom of \( BC \) at the limit of a vanishingly small internuclear separation.

By removing, for a given tritonic geometry, the sum of the two-body energy terms from the corresponding interaction energies, one obtains the total three-body energy. By then subtracting the three-body dynamical correlation contribution in equation (15) from the total three-body energy, the three-body EHF energy contribution
\[ P^{(j)}(Q_1, Q_2, Q_3) = C_4^{(j)} + C_2^{(j)} Q_1 + C_3^{(j)} Q_3 + C_4^{(j)} Q_1^2 + C_5^{(j)} S_{2a} + C_6^{(j)} Q_4 Q_3 \]
\[ + C_7^{(j)} S_{2a}^2 + C_8 Q_3^2 + C_9^{(j)} Q_1 S_{2a}^2 + C_{10}^{(j)} S_{3a}^2 + C_{11}^{(j)} Q_4^2 Q_3 + C_{12}^{(j)} Q_1 S_{2a}^2 \]
\[ + C_{13}^{(j)} Q_3 S_{3a} + C_{14}^{(j)} Q_1^2 + C_{15}^{(j)} Q_1 S_{2a}^2 + C_{16}^{(j)} S_{2a}^2 + C_{17}^{(j)} Q_1 S_{3a} \]
\[ + C_{18}^{(j)} Q_1 Q_3 + C_{19}^{(j)} Q_1 S_{2a}^2 + C_{20}^{(j)} Q_1 Q_3 S_{2a}^2 + C_{21}^{(j)} Q_4 S_{2a}^2 + C_{22}^{(j)} Q_3 S_{3a}^2 + C_{23}^{(j)} Q_1 S_{3a}^2 \]
\[ + C_{24}^{(j)} Q_1^2 S_{3a} + C_{25}^{(j)} Q_1 S_{2a} S_{3a} + C_{26}^{(j)} Q_3 S_{3a} + C_{27}^{(j)} S_{2a} S_{3a} \]
\[ + C_{28}^{(j)} Q_3 Q_4 + C_{29}^{(j)} Q_4 S_{3a} + C_{30}^{(j)} Q_4 Q_3 S_{2a} + C_{31}^{(j)} Q_3 S_{2a} S_{3a} \]
\[ + C_{32}^{(j)} Q_1 S_{2a}^2 S_{3a} + C_{33}^{(j)} Q_3 S_{2a} S_{3a} + C_{34}^{(j)} S_{2a}^2 S_{3a}^2 + C_{35}^{(j)} Q_4^2 S_{3a}^2 + C_{36}^{(j)} Q_4 S_{3a} S_{3a} \]
\[ + C_{37}^{(j)} Q_3^2 S_{3a}^2 + C_{38}^{(j)} Q_3 S_{3a} S_{3a} + C_{39}^{(j)} Q_4 S_{3a} S_{3a} + C_{40}^{(j)} S_{2a} S_{3a} + C_{41}^{(j)} S_{3a} \]
\[ + C_{42}^{(j)} Q_3^2 + C_{43}^{(j)} Q_4^2 S_{3a} + C_{44}^{(j)} Q_3^2 S_{3a} + C_{45}^{(j)} Q_4^2 S_{3a} \]
\[ + C_{46}^{(j)} Q_3^2 S_{3a}^2 + C_{47}^{(j)} Q_4 S_{3a} S_{3a} + C_{48}^{(j)} Q_3^2 S_{3a}^2 + C_{49}^{(j)} Q_3^2 S_{3a} S_{3a} \]
\[ + C_{50}^{(j)} S_{2a} S_{3a} \] 

In turn, \( R_{1,ref}^{(j)} \) is a reference geometry, and \( \gamma_{1}^{(j)} \) nonlinear range-determining parameters that have been optimized by trial-and-error such as to minimize the root-mean-square deviation (rmsd) error while warranting the proper asymptotic behavior on dissociation. The complete set of parameters totals 150 linear coefficients, 9 nonlinear ones, and 9 reference bond distances. Table S3 of the SI gathers the reference geometries and nonlinear range-determining parameters, while Table S4 of the SI collects the linear ones. The rmsd of the final DMBE/CBS PES with respect to all fitted ab initio energies are given in Table 2. As shown, the DMBE/CBS form fits regions up to the collinear and bending barrier (32 kcal mol\(^{-1}\) above the H...HF van der Waals minima) with rmsd smaller than 0.65 kcal mol\(^{-1}\) and a maximum unsigned deviation of <2.7 kcal mol\(^{-1}\).

### Table 2. Accumulated (acc.) and stratum (str.) root-mean-square deviations (in kcal mol\(^{-1}\)) of DMBE PES.

<table>
<thead>
<tr>
<th>Energy</th>
<th>( N^a ) max. dev. ( b ) rmsd</th>
<th>( N_{str,mst} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0–10</td>
<td>254</td>
</tr>
<tr>
<td>20</td>
<td>10–20</td>
<td>325</td>
</tr>
<tr>
<td>40</td>
<td>20–40</td>
<td>1021</td>
</tr>
<tr>
<td>60</td>
<td>40–60</td>
<td>1308</td>
</tr>
<tr>
<td>80</td>
<td>60–80</td>
<td>1441</td>
</tr>
<tr>
<td>100</td>
<td>80–100</td>
<td>1639</td>
</tr>
<tr>
<td>120</td>
<td>100–120</td>
<td>1804</td>
</tr>
<tr>
<td>140</td>
<td>120–140</td>
<td>1875</td>
</tr>
</tbody>
</table>

\( a \) Number of calculated MRCI(Q)/CBS points up to the indicated energy range.

\( b \) Maximum deviation up to the indicated energy range.

\( c \) Number of calculated MRCI(Q)/CBS points with an energy deviation larger than the root-mean-square deviation.

is obtained. This has been modeled via the three-body distributed-polynomial [64,70] form

\[ V_{EHF}^{(3)} = \sum_{j=1}^{3} \left\{ P^{(j)}(Q_1, Q_2, Q_3) \right\} \times \prod_{i=1}^{3} \left\{ 1 - \tanh \left[ \gamma_{i}^{(j)} \left( R_i - R_{i,ref}^{(j)} \right) \right] \right\} \]

where \( P^{(j)}(Q_1, Q_2, Q_3) \) is the \( j \)-th polynomial defined as see equation (19) above

where \( S_{2a} = Q_2^2 + Q_3^2, S_{2b} = Q_2^2 - Q_3^2, \) and \( S_{3} = Q_3^3 - 3Q_2^2Q_3, \) with \( Q_i (i = 1 - 3) \) being symmetry coordinates defined as [70–73]

\[
\begin{bmatrix}
Q_1 \\
Q_2 \\
Q_3
\end{bmatrix} = \begin{bmatrix}
\sqrt{1/3} & \sqrt{1/3} & \sqrt{1/3} \\
\sqrt{1/2} & -\sqrt{1/2} & 0 \\
-\sqrt{1/6} & -\sqrt{1/6} & 2/3
\end{bmatrix}
\begin{bmatrix}
R_1 - R_{1,ref}^{(j)} \\
R_2 - R_{2,ref}^{(j)} \\
R_3 - R_{3,ref}^{(j)}
\end{bmatrix}
\]

### 4 Features of FH\(_2\) potential energy surface

We have located and analyzed the stationary points of the new DMBE/CBS PES for FH\(_2\) (1.2\(^{\pm}A\)), including transition states and van der Waals wells in the entrance
channel. Table 3 compares the attributes of the stationary points (geometry, energy, and vibrational frequencies) for the \( F + H_2 \) reaction of \( FH_2 \). DMBE/CBS PES with the other theoretical and experimental results. As seen from Table 3, there is a wide amplitude on the values for the collinear energy barrier, which is quite sensitive to wave functions, basis sets, and electron correlation effects, and indeed this results on an extensive effect on the barrier heights of the collinear and bent transition state geometry for this reaction is linear. Here, we find the classical barrier height lying above the classical barrier height lying above the experimental value of 32 kcal mol\(^{-1}\)).

Figures 1–7 illustrate the major topographical features of the present DMBE/CBS PES. Clearly, it has a smooth and correct behavior over the whole configuration space. Also visible from these plots are its major stationary points: the collinear and also the bent transition states for the \( F + H_2 \) reaction, the \( C_{2v} \) saddle point, the energy barrier for the \( H^+ + FH \rightarrow H + FH^+ \) exchange reaction, and the van der Waals minima. Figure 1 shows a contour plot for HH and FH stretching at the \( H - H - F \) linear configuration. The notable feature from this figure is the collinear transition state. In turn, Figure 2 shows a contour plot for the \( C_{2v} \) insertion of F into \( H_2 \). Visible from this plot are the \( F - H_2 \) van der Waals minimum, the \( C_{2v} \) saddle point, and the transition state for the \( H^+ + FH \rightarrow H + FH^+ \) exchange reaction. As already predicted by other works [20,25,31,74–76], the transition state geometry for this reaction is linear. Here, we find the barrier of this transition state to be located at a geometry with \( R_{FH} = 2.147 \) a\( \)\( o \) and \( R_{HH} = 4.294 \) a\( \)\( o \), with the classical barrier height lying 40.4 kcal mol\(^{-1}\) above the \( H + FH \) asymptote. As shown from Table 4, the value of

### Table 3. Comparison of saddle point properties for the \( F + H_2 \) reaction.

<table>
<thead>
<tr>
<th>Feature</th>
<th>( R_{{FH/a0}} )</th>
<th>( R_{{HH/a0}} )</th>
<th>( \theta_{{FHH/deg}} )</th>
<th>( \Delta E^{#} )</th>
<th>( \omega_1 )</th>
<th>( \omega_2 )</th>
<th>( \omega_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collinear transition state</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMBE(^b)</td>
<td>3.020</td>
<td>1.426</td>
<td>180</td>
<td>2.301</td>
<td>3924</td>
<td>314</td>
<td>594(i)</td>
</tr>
<tr>
<td>FXZ [17]</td>
<td></td>
<td>180</td>
<td>2.222</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5SEC [24]</td>
<td>3.170</td>
<td>1.440</td>
<td>180</td>
<td>1.57</td>
<td>3935</td>
<td>317</td>
<td>390(i)</td>
</tr>
<tr>
<td>SW [31]</td>
<td>2.950</td>
<td>1.442</td>
<td>180</td>
<td>1.92</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASW [98]</td>
<td>2.936</td>
<td>1.442</td>
<td>180</td>
<td>1.971</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BWLTJ [30]</td>
<td>2.950</td>
<td>1.450</td>
<td>180</td>
<td>1.66</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>SCU [99]</td>
<td>2.913</td>
<td>1.446</td>
<td>180</td>
<td>2.05</td>
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<td></td>
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<tr>
<td>WKLW [100]</td>
<td>2.801</td>
<td>1.451</td>
<td>180</td>
<td>1.78</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LWA-5 [33]</td>
<td>2.936</td>
<td>1.443</td>
<td>180</td>
<td>1.773</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LWA-78 [33]</td>
<td>2.954</td>
<td>1.439</td>
<td>180</td>
<td>1.662</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bent transition state</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMBE(^b)</td>
<td>3.097</td>
<td>1.414</td>
<td>112</td>
<td>1.768</td>
<td>4220</td>
<td>701</td>
<td>509(i)</td>
</tr>
<tr>
<td>FXZ [17]</td>
<td></td>
<td></td>
<td>1.770</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5SEC [24]</td>
<td>3.100</td>
<td>1.430</td>
<td>104</td>
<td>0.97</td>
<td>4142</td>
<td>428</td>
<td>379(i)</td>
</tr>
<tr>
<td>SW [31]</td>
<td>2.922</td>
<td>1.457</td>
<td>119</td>
<td>1.53</td>
<td>3873</td>
<td>131</td>
<td>115(i)</td>
</tr>
<tr>
<td>ASW [98]</td>
<td>2.919</td>
<td>1.456</td>
<td>116</td>
<td>1.545</td>
<td>3883</td>
<td>105</td>
<td>109(i)</td>
</tr>
<tr>
<td>LWA-5 [33]</td>
<td>2.942</td>
<td>1.455</td>
<td>113</td>
<td>1.259</td>
<td>3933</td>
<td>172</td>
<td>102(i)</td>
</tr>
<tr>
<td>LWA-78 [33]</td>
<td>2.961</td>
<td>1.452</td>
<td>113</td>
<td>1.091</td>
<td>3984</td>
<td>152</td>
<td>101(i)</td>
</tr>
<tr>
<td>( C_{2v} ) second-order saddle point</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMBE(^b)</td>
<td>2.324</td>
<td>2.185</td>
<td>57.9</td>
<td>15.82</td>
<td>2859</td>
<td>3637(i)</td>
<td>1505(i)</td>
</tr>
</tbody>
</table>

\(^{a}\) Relative to the \( F + H_2 \) asymptote (in kcal mol\(^{-1}\)).

\(^{b}\) From global DMBE/CBS PES.

### Table 4. Comparison of transition state attributes for the \( F + H_2 \) exchange reaction.

<table>
<thead>
<tr>
<th>Feature</th>
<th>( R_{{FH/a0}} )</th>
<th>( \theta_{{FH/deg}} )</th>
<th>( \Delta E^{#} )</th>
<th>( \omega_1 )</th>
<th>( \omega_2 )</th>
<th>( \omega_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMBE(^b)</td>
<td>2.147</td>
<td>180</td>
<td>40.42</td>
<td>2206</td>
<td>314</td>
<td>2748(i)</td>
</tr>
<tr>
<td>SW [31]</td>
<td>2.12</td>
<td>180</td>
<td>41.11</td>
<td>2333</td>
<td>337</td>
<td>4425(i)</td>
</tr>
<tr>
<td>ASW [98]</td>
<td>2.12</td>
<td>180</td>
<td>41.13</td>
<td>2351</td>
<td>401</td>
<td>4361(i)</td>
</tr>
<tr>
<td>LWA-5 [33]</td>
<td>2.15</td>
<td>180</td>
<td>41.52</td>
<td>2377</td>
<td>336</td>
<td>314(i)</td>
</tr>
<tr>
<td>LWA-78 [33]</td>
<td>2.16</td>
<td>180</td>
<td>42.00</td>
<td>2420</td>
<td>242</td>
<td>2673(i)</td>
</tr>
</tbody>
</table>

\(^{a}\) Relative to the \( FH + H \) asymptote (in kcal mol\(^{-1}\)).

\(^{b}\) From global DMBE/CBS PES.
are the two equivalent asymmetric F$\text{–}H$–H configurations. Such a transition state is visible from Figure 5 are the two equivalent asymmetric F$\text{–}H$–H configurations. Contours are equally spaced by 0.015$E_h$, starting at $-0.2229E_h$.

Figure 1. Contour plot for bond stretching in linear F$\text{–}H$–H configurations. Contours are equally spaced by 0.01$E_h$, starting at $-0.22E_h$.

Figure 2. Contour plot for the $C_{2v}$ insertion of the F atom into $H_2$. Contours are equally spaced by 0.01$E_h$, starting at $-0.1747E_h$.

40.86 kcal mol$^{-1}$ predicted from the DMBE/CBS PES is only 0.69 kcal mol$^{-1}$ lower than the one obtained by Stark and Werner [31]. Such a transition state is visible from Figure 3, which shows a contour plot for FH stretching at a H$\text{–}F$–H linear configuration. Visible from Figure 3 are the two equivalent asymmetric F$\text{–}H_2$ van der Waals saddle points (see Tab. 5), which are separated by the barrier for F-atom-exchange lying halfway between them.

Figure 4 shows a contour plot for a F atom moving around a HH diatom with the bond length fixed at $R_{HH} = 1.401$ a$_0$. Note the van der Waals valley, with two minima: one at a geometry with $C_{2v}$ symmetry, the other having $C_{scw}$ symmetry. In turn, Figure 5 shows a contour plot for a H atom moving around a FH diatom with the bond length fixed at $R_{FH} = 1.742$ a$_0$. The two plots clearly reveal a smooth behavior both at short- and at long-range regions. It is also visible Figure 5 are the the H...HF and H...FH van der Waals minimum, and a van der waals transition state connecting mentioned above two minimum (see Tab. 6).

Figure 6 shows the isotropic and leading anisotropic components of the F$\text{–}H_2$ interaction potential, two important quantities of relevance in atom-diatom scattering [77]. Specifically, the isotropic potential $V_0$ determines

<table>
<thead>
<tr>
<th>Feature</th>
<th>$C_{2v}$ min.</th>
<th>$C_{scw}$ min.</th>
<th>$C_s$ s.p.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1/a_0$</td>
<td>1.4292</td>
<td>1.3998</td>
<td>1.3999</td>
</tr>
<tr>
<td>$R_2/a_0$</td>
<td>4.3879</td>
<td>6.0370</td>
<td>5.8532</td>
</tr>
<tr>
<td>$R_3/a_0$</td>
<td>4.3879</td>
<td>7.4368</td>
<td>7.0213</td>
</tr>
<tr>
<td>$\Delta V^c$</td>
<td>$-0.5119$</td>
<td>$-0.0897$</td>
<td>$-0.0772$</td>
</tr>
<tr>
<td>$\omega_1$ (intra)/cm$^{-1}$</td>
<td>4334</td>
<td>4438</td>
<td>4419</td>
</tr>
<tr>
<td>$\omega_2$ (inter)/cm$^{-1}$</td>
<td>471</td>
<td>111</td>
<td>91</td>
</tr>
<tr>
<td>$\omega_3$ (bend)/cm$^{-1}$</td>
<td>234</td>
<td>93</td>
<td>82</td>
</tr>
</tbody>
</table>

a Van der Waals minimum.
b Saddle point connecting the two van der Waals minima.
c Relative to the F$\text{+}H_2$ asymptote (in kcal mol$^{-1}$).
lying along the $X$-axis with the center of the bond fixed at the origin. Contours are equally spaced by 0.001 $E_h$, starting at $-0.1744747 E_h$. Shown in dash are contours equally spaced by $-0.00005 E_h$, starting at $-0.1744747 E_h$.

Fig. 4. Contour plot for a F atom moving around a H$_2$ molecule fixed at the equilibrium geometry $R_1 = 1.401$ a$_0$ and lying along the $X$-axis with the center of the bond fixed at the origin. Contours are equally spaced by 0.005 $E_h$, starting at $-0.22291 E_h$. Shown in dash are contours equally spaced by $-0.000035 E_h$, starting at $-0.22291 E_h$.

Fig. 5. Contour plot for a H atom moving around a FH molecule fixed at the equilibrium geometry $R_{FH} = 1.742$ a$_0$ and lying along the $X$-axis with the center of the bond fixed at the origin. Contours are equally spaced by 0.005 $E_h$, starting at $-0.22291 E_h$. Shown in dash are contours equally spaced by $-0.000035 E_h$, starting at $-0.22291 E_h$.

Fig. 6. Isotropic ($V_0$) and leading anisotropic ($V_2$) components of the $F - H_2$ interaction potential, with the diatomic molecule fixed at the equilibrium geometry. Continuous line, DMBE; dashed line, three-body dynamical correlation term (leading to atom-diatom dispersion interaction at large distances) in dashed line, three-body dynamical correlation term (leading to atom-diatom dispersion interaction at large distances) in equation (15). The axes in all panels have the same units.

Table 6. Attributes of H...HF and H...FH van der Waals stationary points.

<table>
<thead>
<tr>
<th>Feature</th>
<th>H...HF min.</th>
<th>H...FH min.</th>
<th>$C_s$, s.p.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1/a_0$</td>
<td>4.1038</td>
<td>7.1935</td>
<td>6.7793</td>
</tr>
<tr>
<td>$R_2/a_0$</td>
<td>1.7513</td>
<td>1.7397</td>
<td>1.7492</td>
</tr>
<tr>
<td>$R_3/a_0$</td>
<td>5.8551</td>
<td>5.4538</td>
<td>5.9349</td>
</tr>
<tr>
<td>$\Delta V^c$</td>
<td>$-0.3615$</td>
<td>$-0.1555$</td>
<td>$-0.0924$</td>
</tr>
<tr>
<td>$\omega_1$ (intra)/cm$^{-1}$</td>
<td>4132</td>
<td>4165</td>
<td>4216</td>
</tr>
<tr>
<td>$\omega_2$ (inter)/cm$^{-1}$</td>
<td>142</td>
<td>67</td>
<td>63i</td>
</tr>
<tr>
<td>$\omega_3$ (bend)/cm$^{-1}$</td>
<td>235</td>
<td>69</td>
<td>95</td>
</tr>
</tbody>
</table>

*a Van der Waals minimum.

*b Saddle point connecting the two van der Waals minima.

*c Relative to the H + FH asymptote (in kcal mol$^{-1}$).

how close on average the atom and molecule can approach each other. A spherically averaged long range potential for F + H$_2$ has been determined experimentally from scattering data by Aquilanti et al. [78]. The well depth of $V_0$ is predicted from our DMBE PES to be 54.1 cm$^{-1}$, in quite satisfactory agreement with the empirical value of 75.8 cm$^{-1}$ [78] and theoretical result of 72.5 cm$^{-1}$ [31]. Its location is here predicted at 5.11 a$_0$ (see the insert of Fig. 6), thus falling only somewhat shorter than the theoretical value [31] of 5.30 a$_0$ and the empirical counterpart [78] of 5.58 a$_0$. Note that spin-orbit effects have been ignored, and hence any agreement with experiment should be viewed with caution. In turn, the magnitude of $V_2$ indicates whether or not the molecule prefers to orient its axis along the direction of the incoming atom: a negative value favors the collinear approach while a positive value favors the approach through an isosceles triangular geometry. Thus, the positive $V_2$ at distances larger than 3.43 a$_0$ but smaller than 6.46 a$_0$ (see the insert of Fig. 6) favors the approach through an isosceles triangular geometry. This conforms with the fact that the deepest well is associated with the T-shaped van der Waals structure.

All major topographical features of the PES are probably better viewed in the relaxed triangular plot [79] of Figure 7 utilizing scaled hyperspherical coordinates ($\beta^* = \beta/Q$ and $\gamma^* = \gamma/Q$):

$$
\begin{pmatrix}
Q \\
\beta \\
\gamma
\end{pmatrix} =
\begin{pmatrix}
1 & 1 & 1 \\
0 & \sqrt{3} & -\sqrt{3} \\
2 & 1 & -1
\end{pmatrix}
\begin{pmatrix}
R_1^2 \\
R_2^2 \\
R_3^2
\end{pmatrix}.
$$

Visible are the equivalent stationary structures corresponding to the collinear transition state, the bent transition state for F + H$_2$, the energy barrier for the H$^+$ + FH $\rightarrow$ H + FH$'$ exchange reaction as well as other stationary points.

Finally, preliminary integral cross section calculations have been carried out for the reaction F$(^3\Sigma^+_g)$ +
be written as
\[ \hat{H} = -\frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu_r} \frac{\partial^2}{\partial r^2} + \frac{(J-j)^2}{2\mu_R R^2} + \frac{j^2}{2\mu_r r^2} + V \]  

(23)

where \( \mu_R \) and \( \mu_r \) are the corresponding reduced masses for the radial Jacobi coordinates, respectively. \( J \) is the total angular momentum operator, and \( j \) is the rotational angular momentum operator of the BC diatomic molecule in the reaction \( A + BC \rightarrow AB + C \).

By substitution of the scattering matrix in the helicity representation into the standard formulas, we obtain for the total integral cross section \[91\]
\[ \sigma_{\nu j \to \nu' j'} = \frac{\pi}{(2j_0 + 1)\times L}\left| \sum_{\nu} \sum_{K_0} \sum_{J} (2J + 1) \right| S_{\nu j \to \nu' j'}^{J} \left| K_0 \right|^2 \]  

(24)

with the total differential cross section assuming the form \[91\]
\[ \frac{d\sigma_{\nu j \to \nu' j'}(\theta, E)}{d\Omega} = \frac{1}{2j_0 + 1} \times \left( \sum_{\nu} \sum_{K_0} \sum_{J} (2J + 1) \right) d_{\nu j \to \nu' j'}^{J} \left| K_0 \right|^2 \]  

(25)

where \( \theta \) is the scattering angle between the incoming reactants and the scattered products.

Figure 8 compares the initial state-specified \((\nu = 0, j = 0)\) total ICSs as calculated with QCT and QM methods as a function of the collision energy. The cross section shows a typical threshold behavior and increases monotonically with energy due to the energy barrier along the minimum energy path. Also shown in Figure 8 are the ICSs calculated with QCT method on the 6SEC and T5A PESs of Rosenman et al. \[92,93\]. It is seen that the ICSs based on our surface smaller than the results based on 6SEC. Along the range of collision energies from 1.4 to 4.5 kcal mol\(^{-1}\) the ICSs from our PES are larger than the results based on 6SEC. This trend is the opposite when the collision energies larger than 4 kcal mol\(^{-1}\). Because of existence of a barrier along the minimum energy path on the three PESs, threshold exists in all integral cross sections as shown in Figure 8. The threshold of our results is large due to the higher energy barrier of our DMBE PES comparing with THE other two PESs. We further observe from Figure 8 that our QM results are consistent with the QCT ones in the range of higher collision energies. In fact, the main difference between the QCT and QM results is seen to be in the threshold region, where tunneling processes enable QM reactivity to appear at collision energies below the classical barrier. Note that our QM results show oscillations in the range of lower collision energies, which are similar to the ones observed in the reaction \( F + HD \rightarrow HF + D \) by Li et al. \[33\] based on both LWA-5 and LWA-78 PESs, and Skodje et al. \[94\]
based on SW PES. The existence of such oscillations is probably the signature of barrier resonances in which the global scattering wave function interferes with a quasibound state located at linear geometry just beyond the barrier. Of course, information on the rotational and vibrational distributions of the products would be valuable to further assess the title reaction and test the accuracy of the new PES. This analysis will be hopefully addressed in future work.

5 Concluding remarks

A global single-sheeted adiabatic DMBE PES has been reported for the ground state of FH$_2$ on the basis of a least-squares fit to accurate ab initio MRCI + Q energies calculated using AVTZ and AVQZ basis sets subsequently extrapolated to the CBS limit. The various topographical features of the new DMBE/CBS PES have been carefully compared with other realistic PESs from the literature. Based on such features, it is concluded that an accurate description of the FH$_2$ (1$^2\Lambda'$) PES has been achieved. Because the DMBE form here reported fits accurately the ab initio energies, it can both be recommended for dynamics studies of the F + H$_2$ reaction and as a building block for constructing the PESs of larger fluorine/hydrogen containing systems. Finally, exploratory quasi classical trajectory and quantum mechanical calculations are carried out for the F + H$_2$ ($\nu = 0, j = 0$) → FH + H reaction on the new PES showing that it is suitable for any kind of dynamics studies. A detailed report of such studies is planned for a future publication.

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